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14. ABSTRACT
The general approach in the project is to remove intermetallic inclusions from AA2024 surfaces by chemical etching. The procedure is to expose the surface to an oxidant, such as persulfate, in the presence of complexing agents, such as ethylene diamine (EN) and EDTA. The objective is to have the complexing agents attack the oxide, and facilitate the oxidative removal of noble metals from the intermetallic inclusions. In order to monitor this process, we have developed elemental mapping procedures that allow us to use energy dispersive spectroscopy (EDS) to evaluate the effectiveness of the etching process.

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corrosion, electrochemistry, aluminum alloy

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2000 AFOSR Final Technical Report

"New Approaches to Understanding and Preventing Corrosion of Aluminum and Its Alloys"

April 25, 2001

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1. Brief Summary of Research Activities

Our initial efforts in this project centered around use of various spectroscopic methods to study the early events in the inhibition of corrosion pits in AA2024 alloy. Specifically, we applied both Raman and FTIR to examine the amount and nature of chromate-derived species at AA2024 surfaces. This work was briefly described at the Contractors Meeting in Annapolis in 1998.

After extensive discussions with various researchers at that meeting, we significantly changed our approach to the problem. Specifically, we abandoned our efforts to use microscopic spectroscopic techniques to examine the evolution of chromate speciation in pits. This was in large measure because the group at Ohio State (Frankel and McCreery) was fairly far along in their efforts toward this goal. Instead, we redirected our efforts toward the goal of selectively etching the intermetallic inclusions from the AA2024 surface. This dramatic change in our research direction set us back somewhat in terms of productivity. However, as will be seen below, this new direction has been quite fruitful. Our preliminary results with selective chemical etching of intermetallic inclusions were presented at the Contractors Meeting in Florida in January 1999 and also at the Electrochemical Society Meeting in Toronto in Spring 1999. We turn now to a brief discussion of the general approach and recent results in this effort. More detailed results can be found in the presentation that was made available at the 1999 Contractors Meeting. Also, a manuscript was recently submitted to the *Journal of the Electrochemical Society*, and has been through the first round of reviewing. We have submitted a revised version and are awaiting acceptance. A preprint of this manuscript was submitted last Fall as part of our AFOSR reporting requirements.

The general approach to removing intermetallic inclusions from AA2024 surfaces is to expose the surface to an oxidant, such as persulfate, in the presence of complexing agents, such as ethylene diamine (EN) and EDTA. The objective is to have the complexing agents attack the oxide, and facilitate the oxidative removal of noble metals from the intermetallic inclusions. In order to monitor this process, we have developed elemental mapping procedures that allow us to use energy dispersive spectroscopy (EDS) to evaluate the effectiveness of the etching process.

2. Major Accomplishments

The submitted manuscript shows both EDS elemental percentages and backscattering SEM images for surfaces that have been exposed to such etching solutions. These data clearly show that etching occurs, and that the details of the etching solution composition and other factors (e.g. temperature) play a major role in the outcome of the etching process. These results were obtained for the case of baths containing either ethylene diamine (EN) or EN plus EDTA. More recent work suggests that several other types of complexing agents can show significantly different behavior. For example, diethylene triamine (DETA) shows very efficient removal of Cu from the Cu-rich inclusions. This apparently occurs with little corresponding attack at the Al-rich bulk. This etching condition is thus much more selective than any we have observed yet. We are currently completing experiments that delineate the etching behavior of this system, and will report on them in a manuscript to be prepared shortly. During the coming months, we will be writing two papers, one on the DETA results, and one on the use of triethylene tetramine (TETA), another etching agent that is quite selective for Cu removal.

These results are very encouraging, because they demonstrate that it is possible to influence the surface composition of AA2024 in a way that should lead to reduced corrosion susceptibility. One of our goals for the near term will be to examine this susceptibility for AA2024 samples that have been treated using these etching baths.

More recently, we have used the (potentiostatically-controlled) electrochemical reduction of dioxygen at the alloy surface as an assay method for determining the extent to which the chemical etching has removed the inclusions, thereby eliminating the catalytic ability for dioxygen reduction. This has proceeded very nicely, as presented at the January 2001 Contractors Meeting. A manuscript on this study is nearly completed.

3. Technology Transitions

None

4. Personnel supported on the grant

Daniel A. Buttry, PI, 1/2 to 1 month summer
Jesse Seegmiller, Ph. D. graduate student (100%)
Richard Martoglio, Ph. D. graduate student (50%)
Guoying Chen, postdoctoral fellow (50-100%, depending on month)

5. List of Publications

1. "Selective Etching of Intermetallic Inclusions from the Surface of Aluminum AA2024 Alloys", G. Chen, M. Williams, J. Malmberg, J.-S. Kim and D. A. Buttry, submitted to *J. Electrochem. Soc.* (response to reviewers has been submitted, pending final acceptance).
2. "Chemical Heterogeneities in AA2024: Dioxygen Reduction as a Probe of Removal of Cu-Rich Inclusions *via* Chemical Etching", G. Chen, J. Seegmiller and D. A. Buttry, in preparation for *J. Electrochem. Soc.*

6. List of Presentations

1. "Selective Etching of Intermetallic Inclusions from the Surface of Aluminum AA2024 Alloys", G. Chen, M. Williams, J. Malmberg, J.-S. Kim and D. A. Buttry, invited presentation at the Spring Meeting of the Electrochemical Society, Toronto, 2000.
2. "Selective Chemical Etching of Cu-Rich and Fe-Rich Inclusions from the Surface of Aluminum AA2024 Alloys", G. Chen, M. Williams, J. Malmberg, and D. A. Buttry, invited presentation at the Fall Meeting of the Electrochemical Society, Phoenix, 2000.
3. "Chemical Heterogeneities in AA2024: Dioxygen Reduction as a Probe of Removal of Cu-Rich Inclusions *via* Chemical Etching", accepted presentation for the Fall Meeting of the Electrochemical Society, San Francisco, 2001